FRACTURE OF ATOMIC LAYER DEPOSITED TUNGSTEN FILMS

N.R. Moody[1], J. M. Jungk[2], T.M. Mayer[3], R. A. Wind[4], S.M. George[4], W. W. Gerberich[2]
[1]Sandia National Laboratories, Livermore, CA 94550
[2]University of Minnesota, Minneapolis, MN 55455
[3]Sandia National Laboratories, Albuquerque, NM 87158
[4]University of Colorado, Boulder, CO 80309

ABSTRACT

Atomic layer deposited (ALD) films are an ideal choice for enhancing the performance and reliability of microsystem devices. The self-limiting chemistry results in conformal coatings of high aspect ratio structures with monolayer precision. ALD tungsten films are of particular interest for MEMS and LIGA applications due to their good wear resistance. However, property data is extremely limited as most conventional test methods are difficult to apply to these very thin films. We therefore began a study of ALD tungsten films on silicon substrate properties as a function of film thickness using nanoindentation and nanoscratch techniques. Nanoindentation showed that elastic modulus and hardness increased with film thickness. For the thickest films, these values were substantially higher than those of the substrate and hardness equaled values for bulk and sputter deposited films. Of particular concern, nanoscratch tests triggered channel cracking and delamination in the thickest film. These cracks formed in succession during the scratch tests closely following the path established by the previous cracks. Mechanics-based cracking and delamination models showed that the films fractured under steady state conditions at an energy of 0.4 J/m^2. The corresponding interfacial fracture energy for film delamination between the channel cracks was substantially less at 50 mJ/m^2 with a mode I component equal to 30 mJ/m^2. This value is less than the work of adhesion for sputter deposited tungsten films on silicon substrates but may accurately reflect the influence of lower film density along the substrate interface.

1 INTRODUCTION

Low friction and good wear resistance are important factors controlling the performance and reliability of silicon based MEMS and nickel based LIGA structures. While adequate for some applications, as-produced material properties severely restrict use of these structures in many dynamic applications. In addition, the severe geometric constraints of many micromechanical systems and the need to avoid stress gradients make most deposition methods for applying performance enhancing friction and wear-resistance resistance coatings impossible. Atomic layer deposition (ALD) is ideally suited for applying films on high aspect ratio MEMS and LIGA structures. ALD is a chemical vapor deposition process using sequential exposure of reagents with a self-limiting surface chemistry. (Ritala and Leskela [1]) The self-limiting chemistry results in conformal coating of high aspect ratio structures with monolayer precision.

ALD tungsten films are of particular interest for use as MEMS and LIGA coatings due to their high hardness and good wear resistance. However, measurement of mechanical and tribological properties and in particular film resistance to deadhesion presents a significant challenge as most conventional test methods are difficult to apply to very thin films. As a consequence, property data is extremely limited. We have therefore begun a study of ALD tungsten film on silicon substrate properties using nanoindentation techniques to determine mechanical behavior and nanoscratch techniques to measure fracture resistance at small loads characteristic of microsystem operation.

2 MATERIALS AND METHODS

The tungsten films used in this study were deposited using atomic layer deposition at 300˚C onto polished silicon substrates to thicknesses of 1, 5, 10, 50, and 200 nm. A native surface oxide covered the substrate surfaces. The films were nanocrystalline and with a gradient in density that ranged from 80 percent of theoretical value along the substrate interface to full density for thicknesses greater than 4 nm. The range of thicknesses served to highlight the evolution of film and substrate contributions to strength and adhesion.

Nanoindentation was used to determine elastic modulus and hardness values of these films as a function of contact depth using continuous stiffness with a DCM head and 50 nm radius Berkovich diamond indenter on a Nano Indenter XP™. Continuous stiffness was run at 45 Hz at displacement amplitudes of 1 and 2 nm. Nanoscratch tests using a 1 μm radius conical indenter tip were then conducted to determine the scratch resistance for the films. The tests were conducted by simultaneously driving the indenter into the films at a loading rate of 500 μN/s and across the films at a lateral displacement rate of 0.5 μm/s to a maximum load of 100 mN. During each test, the normal and tangential loads and the scratch distance were continuously recorded. The resulting scratch tracks were then examined using optical and scanning electron microscopy.

3 RESULTS

3.1 Mechanical Properties

Nanoindentation showed that elastic modulus and hardness increased with film thickness. The results are shown in Figure 1 where modulus and hardness values are plotted as a function of contact depth. Also shown for comparison are values for sputter deposited tungsten and the mirror polished silicon substrate. For films up to 10 nm thick, the measured moduli tracked substrate values. Values for thicker films were significantly higher than those of the substrate, with the thickest film values exhibiting little substrate influence. Nevertheless, the elastic modulus values were significantly lower than corresponding sputter deposited tungsten films. (Cordill et al. [13]) Hardness of the tungsten films also increased significantly with film thickness. (Figure 1b) However, the near surface decrease in values masks actual property behavior for the thinnest films. Hardness of the thickest film equaled values for sputter deposited films, thereby achieving a primary goal for using this film system.

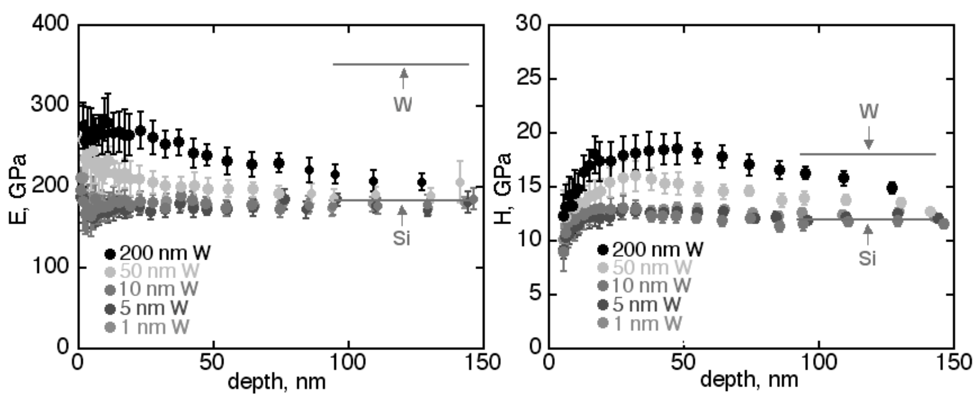

Figure 1. (a) Elastic modulus and (b) hardness increased with film thickness. The values were higher than those of the silicon substrate. Bulk tungsten and silicon substrate values are shown for comparison.

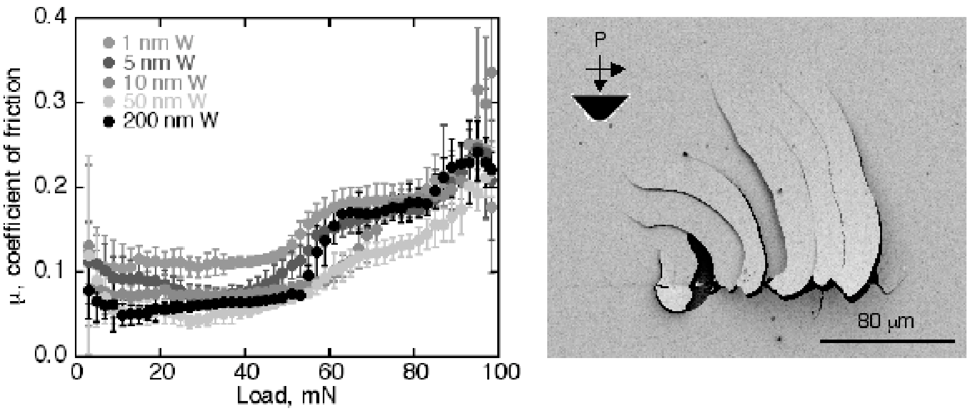

Figure 2. Nanoscratch tests using a conical indenter show that (a) frictional response varied with film thickness. (b) At loads near 50 mN, these tests triggered channel cracking and delamination as shown for the 200 nm thick ALD tungsten film.

3.2 Scratch Tests

A series of nanoscratch tests were conducted on all samples to determine scratch resistance. These tests showed a strong surface effect and marked increase in frictional forces at loads exceeding 40 mN. (Figure 2a) For the 200 nm film, the increase in friction corresponded to extensive channel cracking and delamination. (Figure 2b) The channel cracks initiated at the edge of the scratch track and followed a semi-circular path away from the track eventually becoming parallel to the scratch track. The cracks formed in succession parallel to the path of previous cracks. These cracks were stable and limited in length.

Close examination of scratch tracks strongly suggests that fracture began by film delamination forming circular debonded regions. The channel cracks grew along a path defined by the outer boundary of these debonded regions. The limit of channel crack growth back along a path parallel to the scratch track also appears to correspond to the size of the initial debonded region. Subsequent channel cracks grew along paths parallel to the initial channel crack at a nearly uniform spacing of 19 μm when measured away from the scratch track. A series of scratch tests sampling all orientations shows the same pattern of cracking, the same uniform crack spacing, and initial circular film delamination in all tests.

4 DISCUSSION

Thermal mismatch between the films and native oxide substrate surface layers created by cooling from 300˚C to ambient temperatures led to in-plane residual tensile stresses of 400 MPa determined from corresponding coefficients of thermal expansion. These stresses provided the stored strain energy for film fracture and delamination.

4.1 Film Fracture

Several studies have derived solutions for film and interfacial fracture energies where residual tensile stresses dominate fracture behavior. (Beuth [2]; Beuth and Klingbell [3]; Hu et al. [4]; Hutchinson and Suo [5]; Nakamura and Kamath [6]; Thouless, Cao, and Mataga [7]; Thouless [8]; Thouless, Olsson, and Gupta [9]; Vlassak [10]; Xia and Hutchinson [11]; Ye et al. [12];) These analyses are based on the assumptions that the film and substrate are elastic isotropic solids with dissimilar elastic moduli, the film is subject to a uniform, equibiaxial in-plane tensile stress, and the film thickness is much less than the substrate thickness. When the steady state strain energy release rate is greater than the critical strain energy release for film fracture, crack channeling occurs across the film.

For a through-thickness single channel crack forming in a residually stressed film, the mode I steady state strain energy release rate at fracture, $\mathcal{G}_{Iss}$, is given by, (Hu et al. [4]); Thouless [8]; Beuth [2]; Hutchinson and Suo [5]),

$$\mathcal{G}_{Iss} = \sigma^2 h(1-\nu_f^2)\pi g(\alpha,\beta)/2E_f \tag{1}$$

In this equation, σ is the stress in the film, h is the film thickness, E_f is the elastic modulus of the film, ν_f Poissons ratio for the film, and $g(\alpha,\beta)$ is nondimensionalized integral of the crack opening displacement. (Beuth [2]) The analysis was extended to multiple crack systems to account for crack interaction effects on strain energy release rates and is a function of crack spacing and film thickness. (Thouless [8]; Thouless, Olsson, Gupta [9]; and Hutchinson and Suo [5]). The large spacing to film thickness ratio exhibited by the ALD tungsten film channel cracks show interaction effects are insignificant and eqn (1) therefore defines the film fracture energy. For ALD tungsten on a native silicon dioxide surface layer where α=0.6 and β=0.07, $g(\alpha,\beta)$ is equal to 2.3117. This gives a mode I steady state release rate of 0.4 J/m^2. The corresponding fracture toughness of the film is 0.34 MPa-m$^{1/2}$.

4.2 Delamination

When the fracture energy of the interface is substantially less than the toughness of the film and substrate, channel cracking can trigger interfacial failure. Ye et al. [12] have shown that the mixed mode interfacial strain energy release rate, $\mathcal{G}$, under these conditions is given by,

$$\mathcal{G} = Z_i \sigma^2 h(1-\nu_f^2)/E_f \tag{2}$$

where Z_i is a dimensionless prefactor depending on α and β. Their finite element calculations provided the following approximation for Z_i,

$$Z_i = \frac{1}{2}\left(\frac{\lambda_i}{1+\lambda_i}\right)^{1-2s}\left[1+\beta_3 \exp(-\beta_4\sqrt{\lambda_i})\right] \tag{3}$$

With λ_i=a/h, s=0.654, β_3=0.796, β_4=0.694, and 'a' equal to the delamination half width, Z_i is equal to 0.5 which is typical for stiff films on compliant substrates. (Drory et al. [13]) The interfacial fracture energy is then equal to 50 mJ/m^2. This value is composed of normal mode I and shear mode II contributions with mode I contribution given by the following,

$$\mathcal{G}_I = \mathcal{G}\Big/\left[1+\tan^2\left\{(1-\lambda)\psi\right\}\right] \tag{4}$$

With a phase angle of loading, ψ, equal to 60˚and the material constant, λ, equal to 0.3, the corresponding mode I fracture energy is 30 mJ/m^2. This value is less than the range of mode I values, 0.1 to 0.5 J/m^2, observed for sputter deposited tungsten films on silicon substrates. (Cordill et al. [14]) They are also somewhat lower than film adhesion values measured for CVD films. However, a mode I value of 30 mJ/m^2 may accurately reflect the influence of lower film density along the substrate interface.

5 CONCLUSIONS

We have conducted a systematic study of the mechanical property and fracture behavior of atomic layer deposited tungsten films as a function of film thickness. These films were deposited at 300˚C creating a state of high residual tensile stress. Nanoindentation testing showed that elastic modulus and hardness increased with film thickness. For the thickest films, these values were substantially higher than the substrate values with the hardness equaling values for bulk and sputter deposited films. Nanoscratch tests were then used to study scratch adhesion. These tests triggered channel cracking and delamination in the thickest film. The cracks formed in succession parallel to the path of previous cracks. Corresponding film and interfacial fracture energies were determined using mechanics-based channel cracking and delamination models. For our film system, the analysis showed that film fracture occurred at an energy of 0.4 J/m^2. The corresponding interfacial fracture energy for film delamination between the channel cracks was 50 mJ/m^2 with a mode I component equal to 30 mJ/m^2. This value is less than the work of adhesion for sputter deposited tungsten films on silicon substrates but may accurately reflect the influence of lower film density along the substrate interface.

6 ACKNOWLEDGEMENT

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

7 REFERENCES

[1] Ritala, M., Leskela, M., Atomic Layer Deposition, in Handbook of Thin Films, Nalwa, H. S., ed., ch. 2, vol. 1, Academic Press, San Diego, CA (2001).

[2] Beuth, J. L. Jr., Cracking of thin bonded films in residual tension, Int. J. Solids Structures, 29, 1657-1675 (1992).

[3] Beuth, J. L., Klingbeil, N. W., Cracking of thin films bonded to elastic-plastic substrates, J. Mech. Phys. Solids, 44, 1411-1428 (1996).

[4] Hu, M. S., Evans, A. G., The cracking and decohesion of thin films on ductile substrates, Acta metal., 37, 917-925 (1989).

[5] Hutchinson, J. W., Suo, Z., Mixed mode cracking in layered materials, Advances in Applied Mechanics, 29, 63-191 (1992)

[6] Nakamura, T., Kamath, S. M., Three-dimensional effects in thin film fracture mechanics, Mechanics of Materials, 13, 67-77 (1992).

[7] Thouless, M. D., Cao, H. C., Mataga, P. A., Delamination from surface cracks in composite materials, J. Materials Science, 24, 1406-1412 (1989).

[8] Thouless, M. D., Crack spacing in brittle films on elastic substrates, J. Am. Ceram. Soc., 73, 2144-2146 (1990).

[9] Thouless, M. D., Olsson, E., Gupta, A., Cracking of brittle films on elastic substrates, Acta metal. mater., 40, 1287-1292 (1992).

[10] Vlassak, J. J., Channel cracking in thin films on substrates of finite thickness, Int. J. Fracture, 119/120, 299-323 (2003).

[11] Xia, Z. C., Hutchinson, J. W., Crack patterns in thin films, J.Mech. Phys. Solids, 48, 1107-1131 (2000).

[12] Ye, T., Suo, Z., Evans, A. G., Thin film cracking and the roles of substrate and interface, Int. J. Solids Structures, 29, 2639-2648 (1992).

[13] Cordill, M. J., Bahr, D. F., Moody, N. R., Gerberich, W. W., Recent developments in thin film adhesion measurement, submitted to IEEE Transactions on Device and Materials Reliability (2004).

[14] Drory, M. D., Thouless, M. D., Evans, A. G., On the decohesion of residually stressed thin films, Acta metal., 36, 2019-2028 (1988).